**Simulated-Experimental Cross Validation of Multistage Batch Distillation for Water/Propylene Glycol Separation as Educational Exercise**

Giulia Tonsi\*, Elisa Zanella, Arian Grainca, Andrea Bonetti, Pietro Cassinerio, Carlo Pirola

*Università degli Studi di Milano, Department of Chemistry, Via Golgi 19, 20133, Milan (MI), Italy*

\*giulia.tonsi@unimi.it

Abstract

This study describes an educational exercise concerning the multistage batch distillation of the mixture water-propylen glycol (PG). The research study consisted of three primary components: practical experimentation using a batch distillation setup, computer simulations, utilizing the AVEVA PRO/II™ software, and the development and operation of a multistage system. The initial experiment was centred around the process of distillation involving mixtures of n-heptane/toluene and water/PG. This phase aimed to establish a fundamental understanding that would be crucial for conducting further simulations using the AVEVA PRO/II™ platform. The utilisation of these simulations is the basic background in customizing the design and optimizing the performance parameters of the multistage distillation plant, hence guaranteeing the highest possible level of separation efficiency.

**Keywords**: Simulation software, AVEVA ProII, batch distillation, binary mixture.

* 1. Introduction

Distillation is one of the most used separation technologies. It can be performed in batch or continuous configuration. Batch distillation (M. Mujtaba, 2004) is the most used configuration in educational laboratory and multistage batch distillation represents the higher-level experiment in the education of this separation technique. In the field of chemical engineering, computer simulation is largely used, and it can be a powerful complementary tool for innovative educational lessons. The application of computer simulation to batch distillation is a challenging topic for students, due to the complexity of both vapor liquid interpretation and the in-silico design of these experiments.

The aim of this work is to report the experimental activity for the study of the separation of a binary mixture by batch multistage distillation through the interpretation of the collected data, based on the correct thermodynamic model of fluid phase equilibria involved, and through the correct set-up of the simulation representation. Two different mixtures were tested: one completely organic (n-heptane/toluene) and one composed by water and an organic compound (water/propylene glycol), that is more challenging due to the high latent heat of water evaporation. The experimental plant and methodology, the analysis of the thermodynamic approach for the non-ideal behavior of the mixture and the simulation interpretation will be presented. This didactic methodology embraces the mission of the third-year course titled “Industrial Plant with Laboratory” hold during the Industrial Chemistry Bachelor program at the University of Milano, Chemistry Department. As reported in a previous work of our group (C. Pirola, 2019), the pedagogical objectives of this procedure are mainly related to: the learning of the principles of experimental bench scale plants and the correct experimental procedures, the elaboration of the equilibria data to propose a suitable thermodynamic approach, and the interpretation of the experimental distillations results using a process simulation software (AVEVA PRO/II Simulation datasheet).

* 1. Experimental section
     1. Mono-stage batch distillation

The initial step of this work is the data collection of n-heptane/toluene mono-stage batch distillation. A distillation laboratory scale apparatus has been set up, equipped with: heating mantle to give the required heat for the distillation, round bottom flask of 500 mL, Claisen distillation head for the condensation of the vapour and the control of vapours temperature with a thermocouple, pressure controller and vacuum pump to perform and control under vacuum distillations, round bottom flask with stopcock-equipped-inlet and three-way stopcock-equipped adapter to collect samples in vacuum conditions.

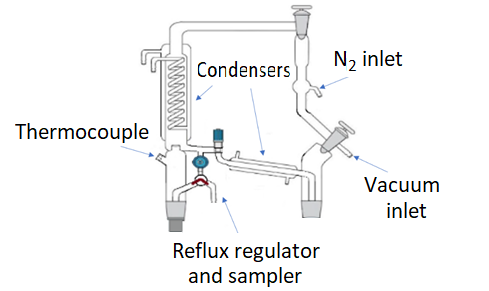
The distillations were conducted as follow:

* In a round bottom flask a certain quantity of n-heptane and toluene was weighed to obtain 100-200 mL of solution of known composition.
* The chosen experimental pressure was set.
* The heating was started to allow the boiling of the mixture.
* Samples of the accumulate distillate were taken at certain intervals time and the composition was determined using gas chromatographic (GC) analysis.

The same apparatus was then used to distil water/propylene glycol (PG) mixtures, in order to evaluate the feasibility of the separation of this mixture, and to further validate the AVEVA PRO/II™ batch simulation setup.

* + 1. Multistage batch distillation

The multistage batch distillation experimental setup was similar to the one described for the mono-stage distillation. A distillation column (h = 35 cm, internal diameter = 3 cm, filled with 0.6 cm ceramic Raschig rings) was added to increase the number of theoretical stages, and equipped with a distillation head (Figure 1) connected directly to the top of the column to allow the setting of the reflux. In the left part, the temperature of the rising vapour was measured by the thermocouple. The vapour was condensed in the top left condenser to allow the liquid to fill the space above the first stopcock. Tuning the two stopcocks was possible to set the quantity of liquid refluxed or taken as distillate, changing the value of R. In the right part the sampling zone and the vacuum and N2 inlet. were located.



***Figure 1****: distillation head scheme*

The experimental procedure used in the multistage distillation process was similar to the one described for the mono-stage distillation with the addition of the setting of the reflux ratio (R). Once the liquid was started to condense in the top left condenser, the two stopcocks were tuned to modify the flow rate of reflux (L) and the flowrate of the distillate (D) to obtain a certain value of R (R=L/D). To measure the R value the left three-ways valve was turned in the position of sampling stopping the reflux of the liquid back into the column. The sampling time was measured to determine the flowrate of L. The values of D were obtained considering the weight of the cuts distilled and the times of sampling. The values of L and D were calculated in mol\*min-1.

* 1. Software simulation section
     1. Mono-stage batch distillation

To start with software simulation the right thermodynamic approach has to be determined using experimental VLE data taken from literature (S. J. Ashcroft et al., 1979; Fendu et al., 2014), and comparing them with the data given by the software using different models (IDEAL, NRTL and UNIQUAC) for the calculation of the activity coefficients.

Firstly, the thermodynamic model, the substances involved, and the unit of measure were set, and then the “batch distillation” unit was selected (Figure 2b). For the mono-stage batch distillation, the settings present in Table 1 were used and the two different operating policies (START UP and CUT-n) followed during the experimental distillation were indicated.

***Table 1****: setting and policies used for the simulation of the mono-stage batch distillation with ProIITM* *(example of simulation data of n-heptane/toluene distillation).*

|  |  |
| --- | --- |
| **ProII COMMAND** | **DESCRIPTION (Example of input data)** |
| **STREAMS** | |
| **Feed** | Flowrate, composition, T and P of the initial mixture (0.754 mol/min, hep/tol=70/30, 20 °C, 760 torr) |
| **Residue** | Content of the still-pot (residue) at the end of the distillation (0.008 mol/min) |
| **Accum-res** | Residue of the condenser holdup (1.04 \* 10-6 mol/min) |
| **Cuts** | All the cuts sampled along the distillation process (number of cuts = 7) |
| **BATCH DISTILLATION WINDOW** | |
| **Number of theoretical stages** | This type of configuration simulates the Claisen distillation with just condenser and reboiler (number of theoretical stages = 2) |
| **Batch cycle time** | This value is used to normalize the exiting flowrates of the unit (cycle time = 1 min) |
| **Initial pressure profile** | Pressure of the distillation (760 torr) and pressure drop in the plant (0 torr per tray) |
| **Liquid holdup** | Holdup in the condenser (0.0001 g) |
| **START UP POLICY** | | | |
| **Charge** | | Liquid charged in the reboiler, and the modalities (100 cm3, instantaneous amount) | |
| **Distil** | | Initial vapor rate of the distillation (3.0 g/min) | |
| **Run until** | | Time for which the policy is kept (10 min) | |
| **CUT-n POLICIES (simulation data for n=1)** | | | |
| **Distil** | | Vapor rate (3.35 g/min, from experimental test) and reflux ratio (R=0) | |
| **Run until** | | Time for which the policy is kept (4 min, from experimental test) | |
| **End cut** | | It indicates the stream to destinate the cut (CUT 1) | |

The simulated data for the different experimental runs conducted were compared with the experimental composition profile to verify and adjust the settings until the best fitting of the data. The same procedure was used for both n-heptane/toluene and water/propylene glycol (PG) mixtures.

* + 1. Multistage batch distillation

The simulations for the two mixtures distilled in the multistage plant were conducted at R = ∞ and R = finite.

In the first case, the simulations for R = ∞ were conducted using a continuous distillation column (Figure 2a) setting a very high reflux ratio (R = 100). It was considered that almost all the product is taken from the bottom of the column, and just a small fraction distilled on top to simulate the sampling. The numbers of separating stages were determined trying different configurations starting from the value obtained with the McCabe and Thiele method (Erich Krell, 1982)). In the case of R=finite, the simulations of the multistage batch plant were similar to the mono-stage batch case, with some additional consideration, both for setting and policies (Table 2).

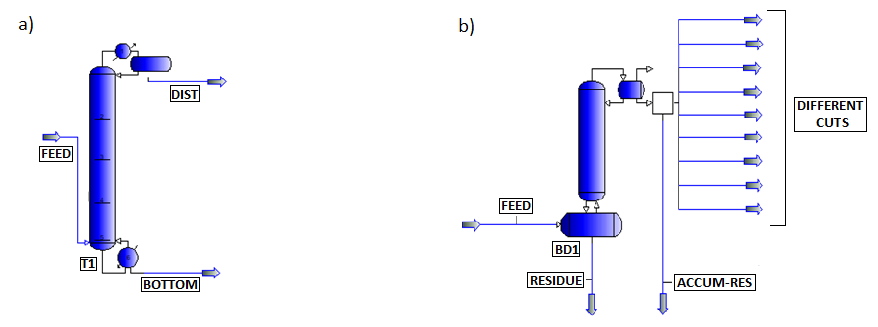
***Table 2****: setting and policies used for the simulation of the multistage batch distillation (R=finite) with AVEVA ProIITM (example of simulation data of water/PG distillation).*

|  |  |  |  |
| --- | --- | --- | --- |
| **ProII COMMAND** | | | **DESCRIPTION (Example of simulation data)** |
| **STREAMS** | | | | |
| **Feed** | | | Flowrate, composition, T and P of the initial mixture (7.753 mol/min, water/PG molar ratio=80/20, 50 °C, 250 torr) |
| **Residue** | | Content of the still-pot (residue) at the end of the distillation (0.001 mol/min) |
| **Accum-res** | | Residue of the condenser hold-up (8.76 \* 10-5 mol/min) |
| **Cuts** | | All the cuts sampled along the distillation process (number of cuts = 12) |
| **BATCH DISTILLATION WINDOW** | | | | |
| **Number of theoretical stages** | | | These values have been estimated starting from the McCabe and Thiele method (number of theoretical stages = 4) | |
| **Batch cycle time** | | | Used to normalize the exiting flowrates of the unit (cycle time = 600 min) | |
| **Initial pressure profile** | | | Pressure of the distillation (250 torr) and pressure drop in the plant (0 torr per tray) | |
| **Liquid holdup** | | | Condenser liquid holdup (4 g) and tray holdup (different values were tried until the best simulation profile was found, 4 g) | |
| **START UP POLICY** | | |
| **Charge** | | Liquid charged in the reboiler, and the modalities (220 g, instantaneous amount) | |
| **Distil** | | Initial vapor rate of the distillation (1.0 g/min) | |
| **Run until** | | Time for which the policy is kept (10 min) | |
| **CUT-n POLICIES (simulation data for n = 1)** | | |
| **Distil** | Top vapor rate (1.25 g/min, from Eq(1)) and reflux ratio (R = 0.5) | |
| **Run until** | Effective experimental distillation times were used, or quantity of distillate taken from every cut (10.018 g) | |
| **End cut** | It indicates the stream to destinate the cut (CUT 1) | |

A parameter that as to be defined is the value of top vapour rate. It was calculated starting from the values of Rmin found with the McCabe and Thiele method and using the Equation (1), where the mean values of D (mol\*min-1) were obtained in the different experimental distillations, while the possible values of L (mol\*min-1) were calculated with the formula of the reflux ratio (R=L/D).

Top vapour rate = L + D (1)

Different values of R were tried until the best simulation profile was obtained.



***Figure 2****: Simulated plants use in PRO II to study a) multistage batch distillation with R=∞ and b) mono and multistage batch distillation with R=finite.*

* 1. Results and discussion

In this section are presented results obtained with the simulation software and the comparison with the experimental data.

From the comparison of the experimental VLE data with the simulated ones using different thermodynamic models the following xy diagrams were obtained. In the case of n-heptane/toluene mixture (Figure 3a), the NRTL model was chosen for the simulation due to its best fitting with the experimental data. For the water/PG mixture instead (Figure 3b), UNIQUAC model showed the lowest error, and so it was chosen for the simulation part of the work.



***Figure 3:*** *Comparison between the experimental values of liquid-vapour equilibria and those simulated on AVEVA ProIITM with the model that best fits the data: a) n-heptane/toluene mixture at 298.15 K, b) water/PG mixture at 383.15 K.*

Using these thermodynamic models, the simulations of the mono-stage distillation were performed. A good fitting of the experimental data was obtained, both in the case of n-heptane/toluene mixture and water/PG one, with a maximum error observed around 3%. In the Figure 4 two examples about the profile comparison for the two mixtures are reported.



***Figure 4****: Comparison of simulated and experimental data obtained with the mono-stage batch distillation: a) n-heptane/toluene mixture, initial molar ratio hept/tol=70/30, p=760 torr and b) Water/PG mixture, initial molar ratio water/PG=70/30, p=255 torr.*

In the case of multistage apparatus, the results obtained from the R = ∞ simulations showed good comparability with the experimental ones (Table 3 confirming the number of separating stages calculated at R = ∞ using McCabe and Thiele method (5-6 trays).

***Table 3****: comparison between experimental and simulated results (for different number of stages) of the R = ∞ distillation of n-heptane/toluene mixtures*

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | **χhept exp** | **χhept sim with 4 trays** | **χhept sim with 5 trays** | **χhept sim with 6 trays** |
| **Dist 1** | **0.706** | 0.571 | 0.639 | **0.695** |
| **Dist 2** | **0.780** | 0.761 | **0.796** | 0.827 |
| **Dist 3** | **0.810** | 0.191 | **0.825** | 0.852 |

Simulations of multistage batch distillation at R = finite are in accord with the experimental results obtained, both in the case of n-heptane/toluene mixture and water/PG one. In Figure 5 two examples about the profile comparison for the two mixtures are reported.



***Figure 5****: comparison of simulated and experimental data for the multistage batch distillation apparatus: a) n-heptane/toluene mix, initial molar ratio hept/tol=20/80, p=760 torr, R=4 and b) water/PG mix, initial molar ratio water/PG=80/20, p=250 torr, R=0.5.*

* 1. Conclusions

This work provides a useful methodology to learn multistage batch distillation optimization procedure, that involves the experimental work on a laboratory scale system, the elaboration of the equilibria data to find the best thermodynamic approach, and the interpretation of the experimental distillations results using a process simulation. Through this procedure, all the set pedagogical objectives mentioned in the introduction section can be achieved. In addition, it is important to notice that the use of simulation software has significant impact in the industrial field, where can lead to significant advantages.

References

S. J. Ashcroft, A. D Clayton, and R. B. Shearn, 1979, Isothermal Vapor-Liquid Equilibria for the Systems Toluene-n-Heptane, Toluene-Propan-2-ol, Toluene-Sulfolane, and Propan-2-ol-Sulfolane, Journal of Chemical and Engineering Data, Vol. 24, No. 3

AVEVA PRO/II Simulation – The Trusted Steady-State Process Simulator. Datasheet

E. M. Fendu\* and F. Oprea, 2014, Vapor−Liquid Equilibria for Water + Propylene Glycols Binary Systems: Experimental Data and Regression, Journal of Chemical and Engineering Data.

E. Krell, 1982, Calculation of separating stages by the McCabe-Thiele method in batch operation, Handbook of laboratory distillation, 2nd edition, 108

M. Mujtaba, 2004, Batch distillation, design, and operation – Series on chemical engineering, Vol.3

C. Pirola, 2019, Learning distillation by a combined experimental and simulation approach in a three steps laboratory, Education for Chemical Engineers, 28, 54–65.